AD-A285 249

REPORT DOCUMENTATION PAGE

Dist. A

Form Approved
OMB No. 0704-0188

2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	FINAL 01 Nov 90 TO 31 Mar 94

4. TITLE AND SUBTITLE

ULTRASTRUCTURE PROCESSING AND PROPERTIES OF HIGH PERFORMANCE

5. FUNDING NUMBERS

AFOSR-91-0078

61102F

2303/CS

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AFOSR-TR- 94 0609

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL
110 Duncan Ave Suite B115
Bolling AFB DC 20332-0001

Dr Lee

OCT 07 1994

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release;
distribution unlimited.

A

12b. DISTRIBUTION CODE

94-31481

13. ABSTRACT (Maximum 200 words)

The proposal was directed towards the fundamental understanding of two areas of polymer materials: 1) Phase Tranformations and Micorstructure, 2) Ultrastructure and Mechanical Properties. Years 1 and 2 were primarily concerned with rigid rod PBX-type materials. During Year 2 and especially in Year 3 emphasis was redirected toward technique development (AFM and LVHRSEM) for materials characterization, and materials processing (roll casting of block copolymers and magnetic field alignment of liquid crystalline polymers). As well, efforts shifted to block copolymer materials during the second half of the grant. Collaborative efforts with Professor P. Prasad at the University of Buffalo (sol-gel composites) and Professors S. Gruner and P. Chaikin at Princeton University (phase transitions and nanolithographic uses of block copolymers) were quite successful.

DTIC QUALITY INSPECTED 2

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
(U)	(U)	(U)	(U)

Final Technical Report
AFOSR 91-0078
"Phase Transformations, Ultrastructure and Properties of Rigid-Rod Fibers."
11/1/90 - 3/31/94

1.0 Abstract

The proposal was directed towards the fundamental understanding of two areas of polymer materials:

1) Phase Transformations and Microstructure
2) Ultrastructure and Mechanical Properties

Years 1 and 2 were primarily concerned with rigid rod PBX-type materials. During Year 2 and especially in Year 3 emphasis was redirected toward technique development (AFM and LVHRSEM) for materials characterization, and materials processing (roll casting of block copolymers and magnetic field alignment of liquid crystalline polymers). As well, efforts shifted to block copolymer materials during the second half of the grant. Collaborative efforts with Professor P. Prasad at the University of Buffalo (sol-gel composites) and Professors S. Gruner and P. Chaikin at Princeton University (phase transitions and nanolithographic uses of block copolymers) were quite successful.

Overall, this grant resulted in 21 publications, with 6 additional papers submitted for publication. 5 graduate students and 5 post-doctoral research associates were fully or partially supported by AFOSR funds.

2.0 Detailed Progress of Researchers Funded By This Grant

In this initial period of this grant we focussed on structure and properties rigid rod materials. We classified the grain boundary structure of rigid rod fibers and experimentally determined the various types of grain boundaries in PBO fibers [1]. The structure of the fibers is known to be influenced by the spinning process and a study of the PBT/PPA/H_2O system demonstrated the key role crystal solvates can play during the coagulations process [2].

Collaborative work on sol-gel prepared PPV-silica composite films helped establish the morphology as a function of processing conditions and for correlation with χ^3 behavior [3].

A novel roll-casting technique was developed during the second year of the grant and applied to diblocks and diblock/homopolymer blends [4,5]. The technique yields extremely highly oriented films of up to 12 cm wide, 4 cm long and 1 mm thick. Such films approximate "single crystals" of hexagonally packed minority component cylinders in the majority matrix (cylindrical diblock composition) or layered films of lamellae. These are nearly structurally perfect specimens and are being used as model materials for physical property measurements. This area is a key area for future exploitation as it contains a good mix of basic science and applied engineering.

In the later portion of the grant period, we also demonstrated controlled organization of block copolymer microdomains in ultra thin films [6]. Here, two-dimensional patterns are formed in films quiescently cast or spin cast. Such structures might potentially be used as templates for nanolithography, at a length scale not easily accessed by electron beam methods.

Building on our grain boundary work in rigid rod materials we undertook an investigation of grain boundary structure in lamellar diblocks. A series of papers [7-9] describe the classification of the two general types of twist and tilt boundaries, their experimental verification via TEM of thin sections, the excellent correspondence with the data of two-dimensional simulation projections using candidate minimal surface models for the grain boundary geometry and justificiation of the various structure by theoretical modeling.

Temperature driven order-order phase transitions in block copolymers were theoretically predicted in 1980 but only in the last two years were any such transitions experimentally observed. We discovered a lamellar to cylindrical transition upon increasing temperature and demonstrated thermal reversibility [10]. Another order-order transition was discovered, in which the high temperature phase was a completely new microdomain morphology: the gyroid [11]. We wrote an invited review on phase morphology in block copolymer systems highlighting order-order transitions for the December, 1993 meeting of the

Royal Society in London [12]. The new gyroid phase is a bicontinuous phase with cubic ($Ia\bar{3}d$, space group #230) symmetry. Much remains to be done in this area to understand the physical properties of the new phase.

We also worked on processing-structure relationships of liquid crystalline polymers. A collaboration with researchers at WPAFB provided an explanation for the image contrast in cholesteric LCPs viewed in TEM and with AFM [13]. Development of uniform texture is an area which needs to be understood in order for LCP materials to realize their great potential as optical materials. We have employed high magnetic fields to align and reorient LCP materials. The development and evolution of Néel inversion walls was successfully followed using light microscopy and AFM [15]. Our approach allowed us to measure the splay and bend elastic constants. Finally, we have helped pioneer low voltage, high resolution SEM to polymer morphology studies [16].

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4.0 Cumulative List of Publications

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